

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 00/00039

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C09D 7/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C09D, C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 53011926 A (JAPAN ATOMIC ENERGY RES INST ET AL) 1978-02-02(abstract)World Patents Index (online). London, U.K.: Derwent Publications, Ltd.(retrieved on 2000-04-25) Retrieved from: EPO WPI Database. DW197811, Accession No. 1978-20539A; JP 53011926 A (JAPAN ATOM ENERGY RES INST) 1978-04-14(abstract).(online)(Retrieved on 2000-04-25). Retrieved from: EPO PAJ Database --	1-16
X	JP 10324842 A (SEKISUI CHEM IND CO LTD) 1998-12-08 (abstract) World Patents Index(online). London, U.K.: Derwent Publications Ltd. (retrieved on 2000-04-25). Retrieved from: EPO WPI Database. DW199908, Accession No. 1999-090203; JP 10324842 A (SEKISUI CHEM CO LTD) 1999-03-31 (abstract).(online)(retrieved on 2000-04-25) Retrieved from: EPO PAJ Database --	1-7,10-16

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"&amp;" document member of the same patent family

Date of the actual completion of the international search

25 April 2000

Date of mailing of the international search report

16-05-2000

Name and mailing address of the ISA

Swedish Patent Office

Authorized officer

## INTERNATIONAL SEARCH REPORT

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PCT/FI 00/00039

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X	EP 0069326 A1 (HOECHST AKTIENGESELLSCHAFT), 12 January 1983 (12.01.83) --	1-7,10-16
X	US 5356714 A (KIRSTEN FRITSCH ET AL), 18 October 1994 (18.10.94) --	1-7,10-16
X	WO 9744335 A1 (EXXON CHEMICAL PATENTS INC.), 27 November 1997 (27.11.97), page 4, line 26 - line 30, Claims --	1-5,8-16
A	US 4522962 A (KIRK J. ABBEY ET AL), 11 June 1985 (11.06.85) --	1-16
A	EP 0781797 A2 (NIPPON PAINT CO., LTD.), 2 July 1997 (02.07.97), Abstract; Examples; Claims --	1-16
A	US 4816500 A (PATRICK H. CORCORAN), 28 March 1989 (28.03.89), column 3, line 59 - line 68; column 4, line 1 - line 6, Abstract; Claims --	1-16
A	GB 953761 A (THE DOW CHEMICAL COMPANY), 2 April 1964 (02.04.64), page 1, line 47 - line 72, Example 1-2 --	1-16
A	US 5017435 A (ROBERT J. BARSOTTI ET AL), 21 May 1991 (21.05.91), column 3, line 39 - line 56, Abstract; Claims -- -----	1-16

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

02/12/99

International application No.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0069326 A1	12/01/83	SE 0069326 T3 DE 3126463 A	20/01/83
US 5356714 A	18/10/94	AT 113646 T DE 4027128 A DE 59103441 D DK 545964 T EP 0545964 A,B SE 0545964 T3 ES 2066459 T JP 6500349 T WO 9203513 A	15/11/94 05/03/92 00/00/00 18/04/95 16/06/93 01/03/95 13/01/94 05/03/92
WO 9744335 A1	27/11/97	AU 3143597 A CA 2254110 A EP 0901481 A US 5878462 A US 5880297 A	09/12/97 27/11/97 17/03/99 09/03/99 09/03/99
US 4522962 A	11/06/85	NONE	
EP 0781797 A2	02/07/97	CA 2194126 A JP 9235487 A US 5747558 A US 5972425 A	29/06/97 09/09/97 05/05/98 26/10/99
US 4816500 A	28/03/89	AT 51886 T AU 604002 B AU 6565386 A BR 8605769 A CA 1292825 A DK 562786 A EP 0225097 A,B SE 0225097 T3 JP 2011327 C JP 7049551 B JP 62129365 A NZ 218385 A	15/04/90 06/12/90 28/05/87 25/08/87 03/12/91 26/05/87 10/06/87 02/02/96 31/05/95 11/06/87 27/01/89
GB 953761 A	02/04/64	NONE	
US 5017435 A	21/05/91	AT 95541 T AU 616022 B AU 3702089 A CA 1339166 A DE 68909721 D,T EP 0355959 A,B JP 2064179 A JP 2690784 B KR 9711342 B MX 166968 B NZ 229683 A	15/10/93 17/10/91 04/01/90 29/07/97 05/05/94 28/02/90 05/03/90 17/12/97 09/07/97 16/02/93 26/03/91

## PCT INTERNATIONAL COOPERATION TREATY

PCT

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NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
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To:

SEPPO LAINE OY  
Itämerenkatu 3 B  
FIN-00180 Helsinki  
FINLANDE

Date of mailing (day/month/year) 08 September 2000 (08.09.00)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference NEST 83 PCT	
International application No. PCT/FI00/00039	International filing date (day/month/year) 18 January 2000 (18.01.00)

## 1. The following indications appeared on record concerning:

☒ the applicant    ☐ the inventor    ☐ the agent    ☐ the common representative

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	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person    ☐ the name    ☒ the address    ☐ the nationality    ☐ the residence

Name and Address NESTE CHEMICALS OY Snellmaninkatu 13 FIN-00170 Helsinki Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 3. Further observations, if necessary:

## 4. A copy of this notification has been sent to:

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The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Jean-Marie McAdams Telephone No.: (41-22) 338.83.38
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## P/INT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

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United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C.20231  
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in its capacity as elected Office

Date of mailing (day/month/year) 04 October 2000 (04.10.00)	
International application No. PCT/FI00/00039	Applicant's or agent's file reference NEST 83 PCT
International filing date (day/month/year) 18 January 2000 (18.01.00)	Priority date (day/month/year) 18 January 1999 (18.01.99)
Applicant SALMI, Maarit et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
10 August 2000 (10.08.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer R. E. Stoffel Telephone No.: (41-22) 338.83.38
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16-05-2000

Name and mailing address of the ISA

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Ellen Setréus/Els

Telephone No. +46 8 782 25 00

## INTERNATIONAL SEARCH REPORT

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PCT/FI 00/00039

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US	4522962	A	11/06/85	NONE	
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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FI

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Helsinki (FI).(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG,  
BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE,  
ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP,  
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MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU,  
SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG,  
US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE,  
LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM,  
AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT,  
BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU,  
MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

*With international search report.**In English translation (filed in Finnish).*

(54) Title: PAINT COMPOSITIONS

(57) Abstract

The present invention concerns a paint composition which comprises a binder, a coalescent agent and optionally admixtures and auxiliary agents known per se. The film forming agent comprises a glycidyl ether or glycidyl ester or a mixture thereof, the hydrocarbyl residue of the alcohol or carboxylic acid, respectively, of the ether or ester comprising a linear or branched, saturated or unsaturated hydrocarbon having 3 to 20 carbon atoms. The invention further concerns a method of accelerating the hardening of paint compositions and a novel method of preparing glycidyl esters. The film forming agents used in the invention lower the film forming temperature better than conventional reactive film forming agents. Due to low volatility the compounds are suitable for no-VOC applications.

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## Paint compositions

The present invention concerns a paint composition according to the preamble of claim 1.

5 Generally, a composition of this kind contains a binder, a coalescent agent and admixtures and auxiliary agents known *per se*.

The invention further relates to a method according to the preamble of claim 14 for accelerating the hardening of a paint composition and to the use according to claim 16.

10  
Many emulsion polymers used in latex paints do not form a film at moderate or low temperatures. In order to enable film formation at these conditions, film forming agents (*coalescent agents*) are added to latex paints. In solvent-borne paints the solvents provide for a lowering of the film formation temperature. The film forming chemicals are often  
15 organic solvents which evaporate into the surrounding air when the paint dries and hardens, thus giving rise to a smell and pollution problem. The traditional film forming agents therefore also increase the amounts of the volatile components (VOC) and the total emissions of the paint.

20 It is an aim of the development of coalescent agents to introduce on the market substituting coalescent agents which do not belong to the group of volatile organic compounds (VOC components). The disadvantage of non-volatile or slowly evaporating components is, however, their plasticising property, which gives rise to slow development of paint film hardness and which may leave the film in a soft condition.

25 Various reactive coalescent agents can be used in paint mixtures which should be kept free from emissions detrimental to the environment. These compounds should react with and form a part of the paint film, whereby the emissions minimized. The aim of using reactive coalescent agents is both to improve the development of the hardness and to reduce the  
30 film formation temperature. These compounds are exemplified by, e.g., different isocyanates and epoxides and siloxanes.

Due to their structure the capability of reactive compounds of reducing the film formation temperature is often very small in comparison to normal volatile or so called no-VOC  
35 coalescent agents. Furthermore, isocyanates are sensitive to moisture and cannot be used in

aqueous dispersions. In order to reach the film formation temperatures required for paints, conventional coalescent agents have to be used in addition to the reactive compounds.

It is an aim of the present invention to eliminate the disadvantages of the prior art and to provide entirely novel paint compositions.

The use of glycidyl esters in solvent-borne paints is known *per se*. Thus, published international patent application WO 97/44335 discloses that glycidyl esters can be used as reactive diluents for the preparation of epoxy, urethane and polyester paints. There is no mention in the publication about other properties of the glycidyl esters, e.g. their capability of forming films.

The present invention is based on the finding that glycidyl derivatives containing a large-sized hydrocarbyl residue, in particular glycidyl ethers and glycidyl esters, have excellent film formation properties and good dispersability in water. According to the invention the coalescent agents of water-borne paint compositions therefore comprise an ether or ester formed by glycidol (2,3-epoxy-1-propanol) and an organic alcohol or carboxylic acid containing 3 to 20 carbon atoms. Surprisingly it has been found that it is possible partially or totally to replace present coalescent agents, in particular reactive coalescent agents, or paint compositions. They make it possible considerably to accelerate the hardening of the paint film.

Glycidyl esters, such as the glycidyl ester of 2-ethylhexanol, can be prepared at high yield and in great purity from the corresponding carboxylic acid by first forming the alkali metal salt of the carboxylic acid, by mixing said salt with a molar excess of epichlorohydrin and by maintaining the reaction mixture at a temperature of at least 60 °C under reflux conditions. The reaction can be continued at said temperature without the formation of significant amounts of by-products, until the yield of the glycidyl ester is at least 80 %.

More specifically, the paint composition according to the present invention is characterized by what is stated in the characterizing part of claim 1.

The method of accelerating the hardening of a paint composition according to the present invention is characterized by what is stated in the characterizing part of claim 14, and the use according to the invention by what is stated in the characterizing part of claim 16.

The invention provides considerable advantages. Thus, the film forming agents according to the invention provide good dispersion of paint compositions which appears to be caused by the weakly polar ether bond or the more polar ester bond. Further, because of the rather large hydrocarbon group of the ether or ester, the novel coalescent agents reduce the film forming temperature better than conventionally used siloxanes or epoxy compounds. Due to the low volatility of the compounds they can be used in so called no-VOC applications. The reactive glycidyl group contained in the compounds makes it further possible to have the coalescent agents react so that they form a part of the paint film, whereby the total emissions are cut and there is an advantageous development of the hardness.

With the compounds it becomes possible to accelerate the hardening of the film so as to attain at least 70 % of the final hardness already within a day. The present glycidyl ethers or esters can be used together with known film forming agents.

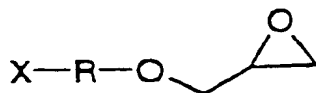
Next, the invention will be examined more closely with the aid of a detailed description and a number of working examples.

The attached drawing shows the development of König-pendulum hardness on glass sheets ( $t=23\text{ }^{\circ}\text{C}$ ,  $rh = 50\%$ ) of Primal E-2955+NPG diglycidyl ether at different temperatures and at a molar ratio between the epoxy and carboxylic acid groups of 0.5 to 1.0.

The present invention uses as a coalescent agent of paint compositions glycidyl ethers and/or esters which contain a linear or branched, saturated or unsaturated hydrocarbyl residue having a hydrocarbyl residue with 3 to 20 carbon atoms, usually 4 to 18 carbon atoms, preferably 4 to 12 carbon atoms, which is linked to the glycidyl group via an ether or ester bond. Short carbon chains give a more rapid development of the hardness and increase the final hardness of the film.

Thus, in the ethers used in the invention, at least one alcohol residue is derived from glycidol (2,3-epoxy-1-propanol), which forms an ether group with a linear or branched monoalcohol, diol, triol, tetraol or pentol having 3 to 20 carbon atoms.

The structure of the preferred glycidyl ethers is depicted in formula I



I

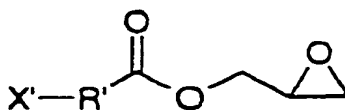
wherein R is a linear or branched, unsaturated or saturated C<sub>3</sub>-C<sub>20</sub> hydrocarbon,  
optionally containing one or several hydroxyl groups, and

X represents hydrogen or a hydroxyl group.

The ether derivatives may contain 1, 2, 3, 4 or 5 glycidyl ether groups. Glycidyl ether groups may also be contained in glycidyl esters which are derived from hydroxyacids. Glycidyl ester compounds derived from diols and polyols may also contain ether groups derived from other alcohols (mixed ethers). In particular, the alcohols of these other alcohols are alkanols, such as lower alkanols (methanol, ethanol, propanol, butanol). The ether groups derived from other alcohols, should such compounds be present, form at the most 80 mole-%, preferably 1 to 50 mole-% of the ether groups of the ether-based coalescent agent.

The other main group of the present coalescent agents is formed by esters which have an alcohol residue derived from glycidol and a carboxylic acid residue derived from a linear or branched carboxylic acid comprising one or several protons (i.e. an acid which contains several carboxylic groups) and having 3 to 20, preferably 4 to 18, in particular 4 to 12 carbon atoms. The multibasic acids provide mono-, di-, tri- etc. esters. The esters can be semiesters or total esters.

The structure of preferred glycidylesters is depicted in formula II



II

wherein R' is a linear or branched, unsaturated or saturated C<sub>2</sub>-C<sub>20</sub>-hydrocarbon, which optionally contains one or several hydroxyl groups, and

X' represents a methyl group, a methylene hydroxy group or a carboxy or lower carboxylate group.

5

Examples of the lower carboxylate groups are, in particular, methoxylate (-COOMe) and ethoxylate (-COOEt).

10

The esters can also be prepared from hydroxy acids, as mentioned above, whereby they may contain ether groups. The glycidyl esters of multibasic acids may contain in addition to the ester group derived from glycidol ester groups derived also from other alcohols (mixed esters). As mentioned above in connection with the ethers, these other alcohols are in particular alkanols, such as lower alkanols, e.g. methanol, ethanol, propanols or butanols.

15

Examples of ethers derived from monoalcohols include 2-ethylhexyl glycidyl ether and octyl glycidyl ether. Ethers derived from dialcohols are represented by mono- and diethers of neopentylglycol and as examples of triethers the triglycidyl ether of trimetanolpropan can be mentioned.

20

As examples of glycidyl esters, 2-ethylhexyl glycidyl ester, octyl glycidyl ester and isopentyl glycidyl ester and as examples of mixed esters the methyl glycidyl ester of gluratic acid can be mentioned.

25

The glycidyl ethers can be prepared by the Williamson ether synthesis starting from epichlorohydrin and alcohols. The preparation of glycidyl ethers has been described in an article by Kida, T., Yokota, M., Masuyama, A. ja Okahara, M., in Synthesis 1993, 487-489. Since the reaction between epichlorohydrin and a hydroxy group releases hydrogen chloride, the etherification is preferably carried out in an alkaline medium which is capable of binding the hydrogen chloride. In the examples below a medium containing potassium hydroxide has been used, whereby the hydrogen chloride forms potassium chloride, which can be separated from the reaction system by filtration. As a solvent of the organic phase in the reaction system, an organic solvent, such as toluene, DMSO or an ether, such as THF, can be used.

35

The etherification is preferably carried out at normal air pressure and at a temperature in

the range of about 0 to 80 °C. Preferably the reaction is carried out at a temperature above room temperature (at above 25 °C) and the temperature is raised after the addition of the reactant in order to increase the reaction rate. The product is recovered from the organic phase by extraction and distillation at reduced pressure.

5

An excess of epichlorohydrin is used in relation to the number of hydroxyl groups. The molar ratio between the epichlorohydrin and the hydroxyl groups of the alcohol is 10:1 - 1:1, preferably 5:1 - 2:1.

10

As far as the invention is concerned, suitable alcohols for the preparation of reactive alkoxides are the below listed monoalcohols and diols and triols. Suitable alcohols are branched or linear monoalcohols, diols and triols comprising generally 3 to 20 (in particular 4 to 18, preferably 4 to 12) carbon atoms. Particularly suitable alcohols for use as starting materials of glycidyl ethers employed in paint compositions are, e.g., 1-butanol, 2-butanol, isobutanol, 1-pentanol, isopentanol, 1-hexanol, 2-ethylhexanol, 1-heptanol, 1-octanol, 2-ethyl-1,3-hexanediol, neopentylglycol, 2-butyl-2-ethyl-1,3-propanediol, trimetylolethane and trimetylolpropane. Other suitable alcohols are 1,4-butanediol, neodecanealcohol, 1,6-hexanediol, 1,10-decanediol and 2-ethyl-2-hexen-1-ol.

15

20

The glycidyl esters according to the invention can be prepared from epichlorohydrin and acids and derivatives thereof e.g. by transesterification by reacting an alkali metal salt, e.g. a sodium salt, of a carboxylic acid with epichlorohydrin. For the dicarboxylic acid the starting materials can comprise, in addition to the acids, also the corresponding anhydride, from which a suitable alkali metal salt is formed. The preparation of glycidyl esters from carboxylic acids is disclosed in an article by Kester, E.B., Gaiser, C.J. and Lazar, M.E., in J. Org. Chem., 8 (1943) 550 and the preparation of alkyl glycidyl esters of anhydrides in an article by Zlatanos, S.N. and Sagredos, A.N., in JAOCS, 67 (1990) 661.

25

The esters can also be prepared by direct esterification.

30

The temperature of the actual esterification reaction is 30 to 120 °C, preferably about 50 to 100 °C. The reaction is carried out at normal air pressure. A catalyst can be used during esterification in an amount of 1 to 40 % of the amount of the esterification agent. Suitable esterification catalysts are p-toluenesulphonic acid, benzenesulphonic acid, sulphuric acid, tin and zinc salts or oxides and titanates. Suitable transesterification catalysts are alkali metal alkoxides, such as potassium or sodium alkoxides, sulphuric acid, hydrochloric acid

35



and acid ion exchange resins.

According to a preferred embodiment the esterification is carried out by first forming an alkali metal salt from a linear or branched, unsaturated or saturated carboxylic acid having 3 to 20 carbon atoms. A reaction mixture is then formed from the alkali metal salt of the carboxylic acid and a molar excess of epichlorohydrin which is refluxed at a temperature of at least 60 °C. Since the reaction mixture contains several components, the reaction temperature can vary, depending on the conditions of the refluxing, even with 20 to 50 degrees. A typical temperature range during the reaction is about 65 to 100 °C. The reaction is continued after this for at least 1 hour at said temperature until the yield of the glycidyl ester is at least 80 %, typically at least 90 %. The formation of the by-products is less than 5 % of the end product, and the purity of the product is over 95 %. During the reaction the excess of epichlorohydrin amounts to at least 50 %, typically the molar ratio of epichlorohydrin to the number of carboxy groups of the reacting carboxylic acid is 2- to 5-fold. Surprisingly it has been found that the glycidyl ester of, e.g. 2-ethylhexanoic acid, can be produced at rather high yield, typically amounting to over 90 % and at high purity (purity in excess of 95 %).

Acids suitable for esterification comprise generally branched or linear mono- or dicarboxylic acids and hydroxy acids having 4 to 18 carbon atoms. Particularly suitable acids as starting compounds of glycidyl esters used in paint compositions are, e.g., butanoic acid, isobutanoic acid, pentanoic acid, isopentanoic acid, 1-hexanoic acid, 2-ethylhexanoic acid, heptanoic acid, octanoic acid, neodecanoic acid, 2-hydroxyisobutanoic acid, 2,2-dimethyl-3-hydroxypropanoic acid, adipinic acid, fumaric acid and maleic acid, succinic acid, glutaric acid and anhydrides and other derivatives thereof and 2-ethyl-2-hexenoic acid, oleic acid and linoleic acid.

The glycidyl ethers and glycidyl esters according to the invention can be formulated into water-borne dispersions, which contain a water-dispersable binder and admixtures and auxiliary agents known *per se*. The binding agents may comprise binders of latex paints, such as poly(vinyl acetate) and polyacrylates. Generally the polyacrylates comprise a synthetic latex, which is an ethylenically unsaturated polymer or copolymer, such as acrylic acid, itaconic acid or maleic acid. The poly(vinyl acetate) may include comonomers having carboxylic groups. Other binders which can be dispersed into water include various water-soluble polymers (e.g. PVA), starch, CMC, hydroxyethyl cellulose and poly(vinyl alcohol).

In addition to the above mentioned binding agents various water-dispersable alkyds may be used. These generally comprise a condensate product formed from a bivalent polyol and fatty acid or a natural oil. To facilitate dispersion or even dissolution in water they typically contain carboxylic acid groups.

5

It is particularly preferred to use the glycidyl ethers and/or esters according to the invention in paint compositions which contains a binder which forms a hard film when the paint has dried. Suitable binders are, e.g. acrylate latexes, wherein styrene is polymerised with one or several acrylate or methacrylate monomers. Latexes of this kind are represented by styrene-  
10 acrylate-latexes having carboxy functions, such as styrene-methylmethacrylate or styrene-butylacrylate latexes. Example 11 below discloses the use of the coalescent agents according to the invention with styrene-ethylacrylate and styrene-2-ethylhexylacrylate-methylmethacrylate. Other suitable latexes which may be mentioned include styrene-2-ethylhexyl acrylate-vinylacetate and styrene-2-ethylhexylacrylate-methylmethacrylate-n-  
15 butylacrylate.

The amount of the binder is generally 20 to 80 % of the dispersion. In mat ceiling and wall paints, as well as in water-borne anticorrosion paints, even smaller amounts can be used. Typically, in commercial latexes, the amount of the actual polymer is about 30 to 60 %, in  
20 particular about 50 %. Since paints may contain as little as only 10 % latex, the amount of polymeric binder in mat paints is only about 5 %. Thus, the paint compositions according to the present invention contain binder in an amount of 3 to 80 %, in particular 4 to 60 %.

The admixtures and auxiliary agents of the dispersions are exemplified by surfactants,  
25 dispersion agents, thickening agents, conservation agents/fungicides, antifoaming agents and fillers and pigments, such as calcium carbonate and titanium dioxide, and pH regulating agents, such as aqueous ammonia.

The amount of reactive coalescent agents according to the present invention in a dispersion  
30 is about 0.01 - 20 wt-%, preferably 0.1 - 15 wt-%. The coalescent agent may be constituted solely by the glycidyl ether, glycidyl ester or a mixture thereof or a mixture of ethers and/or esters and conventional coalescent agents. Generally the portion of glycidyl ethers or esters is at least 20 wt-%, typically over 50 % of the total amount of coalescent agents. Preferably the present glycidyl derivatives are used together with coalescent agents or  
35 mixtures thereof having a boiling point higher than 250 °C at normal air pressure. Coalescent agents of this kind are, e.g. phenyl ethers of ethylene glycol, monoisobutyrate

of 2,2,4-trimethyl-1,3-pentanediol monoisobutyratti (supplied under the trade name Texanol), n-butylether acetate of diethyleneglycol and the mono-n-butyl ether of dipropyleneglycol and the mono-n-butylether of tripropylene glycol (supplied under the trade names Dowanol DpnB and Dowanol TPnB, respectively).

5

The present glycidyl derivatives are capable as such or in combination with known film forming agents considerably to accelerate hardness development of paint compositions. The final hardness is reached already within 7 to 14 days, whereby at least 70 %, in particular at least 80 % and usually at least 90 % of the final film hardness is obtained within 24 hours when at least 20 %, preferably at least 50 %, of the film forming agent of the composition is formed by the glycidyl derivative.

10

As regards stability of the present reactive film forming agents and as far as the use of the paint compositions is concerned, the pH of the paint compositions is preferably neutral or acid, in particular neutral or slightly acidic. In particular the pH of the paint compositions is below about 8.5, preferably below 8.0.

15

The present film forming agents have been compared with commercial products. In paint compositions, the glycidyl compounds of Examples 4, 5 and 9 are capable of reducing the film forming temperature and in this respect they work better than the commercial compounds (Coatosil 1770) used for reference. Tables 1 and 2 will show that the boiling points of many of the prepared glycidyl compounds are in excess of 250 degrees and their volatilization rates are low, whereby their use is safer than of conventional reactive monomers, due to low volatility. The hardness of the paint films develops advantageously for every tested glycidyl compound. Examples 11 studies the development of the König Hardness of the Primal E- 2955+NPG diglycidyl ether on a glass substrate at different temperatures at a molar ratio of the epoxy groups to the carboxy groups of 0.5 to 1.0. At all temperatures, the hardness developed better than that of the 0 samples.

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25

30 The following non-limiting examples illustrate the invention.

**Example 1***Preparation of the glycidyl ether of 2-ethylhexanol*

3 molar equivalents of epichlorohydrin are slowly added to a solution of 1 mol-eq. 2-ethylhexanol and 2 mol-eq of potassium hydroxide in DMSO. The mixture is heated during the addition of epichlorohydrin at about 35 °C and after the addition at 45 °C. The formed KCl salt is filtered and the organic phase is extracted with ether. After drying, the product is distilled at reduced pressure. The purity of the product was 97 % and the yield after distillation 50 % of the theoretical yield.

**Example 2***Preparation of the glycidyl ether of 1-octanol*

3 molar equivalents of epichlorohydrin are slowly added to a solution of 1 mol-eq. 1-octanol and 2 mol-eq. potassium hydroxide in DMSO. The mixture is heated during the addition of epichlorohydrin at about 35 °C and after the addition at 45 °C. The formed KCl salt is filtered and the organic phase is extracted with ether. After drying the product is filtered at reduced pressure. The purity of the product was 100 % and the yield after distillation was 32 % of the theoretical yield.

**Example 3***Preparation of the glycidyl ether of isobutanol*

3 molar equivalents of epichlorohydrin are slowly added to a solution of 1 mol-eq. isobutanol and 2 mol-eq. potassium hydroxide in DMSO. The mixture is heated during the addition of epichlorohydrin at about 35 °C and after the addition at 45 °C. The formed KCl salt is filtered and the organic phase is extracted with ether. After drying the product is filtered at reduced pressure. The purity of the product was 94 % and the yield after distillation was 17 % of the theoretical yield.

**Example 4***Preparation of the diglycidyl ether of neopentylglycol*

3 molar equivalents of epichlorohydrin are slowly added to a solution of 1 mol-eq. neopentyl alcohol and 2 mol-eq. potassium hydroxide in DMSO. The mixture is heated during the addition of epichlorohydrin at about 35 °C and after the addition at 45 °C. The

formed KCl salt is filtered and the organic phase is extracted with ether. After drying the product is filtered at reduced pressure. The purity of the product was 97 % and the yield after distillation was 50 % of the theoretical yield.

5 *Table 1. Properties of the glycidyl ethers prepared in Examples 1 to 4*

Name	Bp (°C)	volatilization rate (ButAc = 1)
Example 1. 2-ethylhexyl glycidylether	221	0.005110
Example 2. octyl glycidylether	255	-
Example 3. isobutyl glycidylether	168	-
Example 4. neopentylglycol diglycidylether	275	0.000387

#### Example 5

##### 10 *Glycidylester of 2-ethylhexyl acid*

From 1 mol-eq. 2-ethylhexanoic acid and 2 mol-eq. NaOH in toluene the sodium salt of the acid was prepared. The water formed was removed with the aid of the toluene by azeotropic distillation. Then the reaction mixture is cooled to 50 °C and 3 mol-eq.  
 15 epichlorohydrin are slowly added. After the addition of the epichlorohydrin the mixture was refluxed for 1 – 8 h at 65 to 100 °C. The epichlorohydrin is removed by distillation and the product is distilled at reduced pressure. The yield of the product after the reaction was 94 % and the purity of the distilled product was 98 %.

#### 20 *Example 6*

##### *Glycidylester of octanoic acid*

From 1 mol-eq. octanoic acid and 2 mol-eq. NaOH in toluene the sodium salt of the acid was prepared. The water formed was removed with the aid of the toluene by azeotropic  
 25 distillation. Then the reaction mixture is cooled to 50 °C and 3 mol-eq. epichlorohydrin are slowly added. After the addition of the epichlorohydrin the mixture was refluxed for 1 – 8 h at 65 to 100 °C. The epichlorohydrin is removed by distillation and the product is distilled at reduced pressure. The yield of the product after the reaction was 24 % and the purity of the distilled product was 90 %.

**Example 7***Glycidylester of isobutanoic acid*

From 1 mol-eq. isobutanoic acid and 2 mol-eq. NaOH in toluene the sodium salt of the acid was prepared. The water formed was removed with the aid of the toluene by azeotropic distillation. Then the reaction mixture is cooled to 50 °C and 3 mol-eq. epichlorohydrin are slowly added. After the addition of the epichlorohydrin the mixture was refluxed for 1 – 8 h at 65 to 100 °C. The epichlorohydrin is removed by distillation and the product is distilled at reduced pressure. The yield of the product after the reaction was 65 % and the purity of the distilled product was 100 %.

**Example 8***Glycidylester of 2,2-dimethyl-3-hydroxypropanoic acid*

From 1 mol-eq. 2,2-dimethyl-3-hydroxypropanoic acid and 2 mol-eq. NaOH in toluene the sodium salt of the acid was prepared. The water formed was removed with the aid of the toluene by azeotropic distillation. Then the reaction mixture is cooled to 50 °C and 3 mol-eq. epichlorohydrin are slowly added. After the addition of the epichlorohydrin the mixture was refluxed for 1 – 8 h at 65 to 100 °C. The epichlorohydrin is removed by distillation and the product is distilled at reduced pressure. The yield of the product after the reaction was 45 % and the purity of the distilled product was 87 %.

**Example 9***Methyl glycidylester of glutaric acid*

1 molar equivalent glutaric anhydride is added to a 1 N solution of NaOH in methanol/toluene. The mixture is cooled and the excess methanol is removed by distillation. The obtained sodium salt of the glutaric acid methyl ester is recrystallized from acetone and dried. 1 molar equivalent of the sodium salt of the glutaric acid and epichlorohydrin are mixed together and refluxed for 1 to 3 hours at 100 to 115 °C. The catalyst may comprise tert-ethylammonium iodide in an amount of 0.02 - 0.1 molar equivalents of the sodium salt. The product mixture is cooled, filtered and the excess epichlorohydrin is removed by distillation. The cooled mixture is extracted with ether and distilled in vacuum. The yield of the product is 72 % and the purity 89 %.

**Example 10***Glycidylester of isopentanoic acid*

From 1 mol-eq. isopentanoic acid and 2 mol-eq. NaOH in toluene the sodium salt of the acid was prepared. The water formed was removed with the aid of the toluene by azeotropic distillation. Then the reaction mixture is cooled to 50 °C and 3 mol-eq. epichlorohydrin are slowly added. After the addition of the epichlorohydrin the mixture was refluxed for 1 – 8 h at 65 to 100 °C. The epichlorohydrin is removed by distillation and the product is distilled at reduced pressure. The yield of the product after the reaction was 77 % and the purity of the distilled product was 96 %.

The boiling point of the isopentanoic acid glycidylester is 226 to 227 °C.

**Table 2.** Properties of the glycidylesters of Examples 5 to 9

Name	Bp (°C)	volatilization rate (ButAc = 1)
Example 5. 2-ethylhexyl glycidylester	242-246	0.001984
Example 6. Octyl glycidylester	190	-
Example 7. Isobutyl glycidylester	69-71 / 0.1 mmHg	-
Example 8. 2,2,dimethyl-3-hydroxypropanoic acid glycidylester	-	-
Example 9. Glutaric acid methylglycidylester	282-283	0.000067

**Example 11**

*Use of the prepared glycidyl compounds as film forming agents in water-based colour compositions.*

The applicability of some of the film forming agents prepared according to Examples 1 to 9 in colour compositions were tested by producing from two different commercial latex dispersion (Joncryl 95 and Primal E-2955) mixtures which contained glycidyl compounds admixed at different concentrations. A commercial film forming agent, viz. epoxysiloxane

(Coatosil 1770) was used for reference. The impact of the various agents on the film forming temperature will appear from the attached table.

*Table 3.* The influence of the glycidyl compounds prepared in Examples 4, 5 and 9 on the film forming temperature of Joncryl-95<sup>®</sup> and Primal E-2955<sup>®</sup> latexes compared with that of a commercial reactive film forming agent (Coatosil 1770) (Joncryl 95 MFFT = 16 °C, dry substance 30 %, Primal E-2995 MFFT = 56 °C\*, dry substance 37 %)

	Joncryl-95 0%	Joncryl-95 3%	Joncryl-95 6%	Primal- 2955 0%	Primal- 2955 3%	Primal- 2955 6%	Primal- 2955 10%
Example 4. Diglycidylether of NPG	16	14	0	40	36	24	15
Example 5. Glycidylester of 2- EHA	16	10	0	40	32	19	11
Example 9. Meth. glycidylester of GA	16	14	0	40	37	28	16
Ref. sample: Coatosil 1770	16	14	10	40	39	33	29

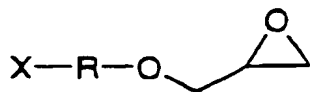
\* Value given by the manufacturer for the dry latex

The attached figure indicates how the König hardness of the Primal E-2955+NPG-dge sample has developed at different temperatures. As the figure shows, the hardness of a sample according to the invention is even up to three times as great as that of a 0 sample.



## Claims:

1. Water-borne paint composition which comprises a binder, a coalescent agent and optionally admixtures and auxiliary agents known *per se*, characterized in that at least 20 % of the film forming agent is formed by a glycidyl ether or glycidyl ester or a mixture thereof, whereby the hydrocarbyl residue of the alcohol or carboxylic acid, respectively, of the ether or ester comprises a linear or branched, unsaturated or saturated hydrocarbon having 3 to 20 carbon atoms.
2. The paint composition according to claim 1, characterized in that it contains 0.01 to 20 wt.-% glycidyl ether and/or ester based on the dry matter content of the composition.
3. The paint composition according to claim 1 or claim 2, characterized in that it contains 3 to 80 wt.-%, in particular 4 to 60 wt.-% of a binder which can be dispersed in water.
4. The paint composition according to claim 3, characterized in that the binder is poly(vinyl acetate), polyacrylate, poly(vinyl alcohol), starch, carboxymethylcellulose, hydroxyethyl cellulose or alkyd.
5. The paint composition according to claim 4, characterized in that the binder forms a hard polymer film when the composition has dried.
6. The paint composition according to any of claims 1 to 5, characterized in that it contains as a coalescent agent a glycidyl ether according to formula I



I

wherein R is a linear or branched, saturated or unsaturated C<sub>3</sub>-C<sub>20</sub> hydrocarbon, optionally containing one or several hydroxyl groups, and

X represents hydrogen or a hydroxyl group.

7. The paint composition according to any of the preceding claims, characterized in that the hydrocarbon residue of the glycidyl ether is derived from 1-butanol, 2-butanol, isobutanol, 1-pentanol, isopentanol, 1-hexanol, 2-ethylhexanol, 1-heptanol, 1-octanol, 2-ethyl-1,3-hexanediol, neopentyl glycol, 2-butyl-2-ethyl-1,3-propanediol, trimethylol ethane, trimethylol propane, 1,4-butanediol, neodecane alcohol, 1-6-hexanediol, 1,10-decanediol or 2-ethyl-2-hexen-1-ol.

8. The paint composition according to any of claims 1 to 4, characterized in that it contains as a film forming agent a glycidyl ester according to formula II



wherein R' is a linear or branched, saturated or unsaturated C<sub>2</sub>-C<sub>20</sub> hydrocarbon, optionally containing one or several hydroxyl groups, and

X represents a methyl group, methylene hydroxy group or a carboxyl or lower carboxylate group.

9. The paint composition according to any of claims 1 to 5 or 8, characterized in that the carboxylic acid residue of the glycidyl ester is derived from butanoic acid, isobutanoic acid, pentanoic acid, isopentanoic acid, 1-hexanoic acid, 2-ethylhexanoic acid, heptanoic acid, octanoic acid, neodecanoic acid, 2-hydroxy-isobutanoic acid, 2,2-dimethyl-3-hydroxypropanoic acid, 2-ethyl-2-hexenoic acid, oleic acid, linolic acid, adipic acid, fumaric acid, maleic acid, succinic acid, glutaric acid or an anhydride or another derivative thereof.

10. The paint composition according to any of the preceding claims, characterized in that the coalescent agent is 2-ethylhexylglycidyl ether, octyl glycidyl ether, mono- or diether of neopentylglycol or triglycidyl ether of trimetanolpropane, or 2-ethylhexyl

glycidyl ester, octyl glycidyl ester or isopentyl glycidyl ester or methyl glycidyl ester of glutaric acid.

11. The paint composition according to any of the preceding claims, c h a r a c t e r i z e d  
5 in that its pH is below about 8.5, preferably below 8.0.

12. The paint composition according to any of the preceding claims, c h a r a c t e r i z e d  
in that it contains in addition to the glycidyl ether and/or ester at least one other coalescent  
agent, the proportion of the glycidyl ether and/or ester of the coalescent agents of the  
10 composition amounting to at least 20 wt.-%, preferably at least 50 wt.-%.

13. The paint composition according claim 12, c h a r a c t e r i z e d in that the other film  
forming agent is the phenyl ether of ethyleneglycol, 2,2,4-trimethyl-1,3-pentanediol  
monoisobutyrate and/or n-butyl ether acetate of diethyleneglycol.

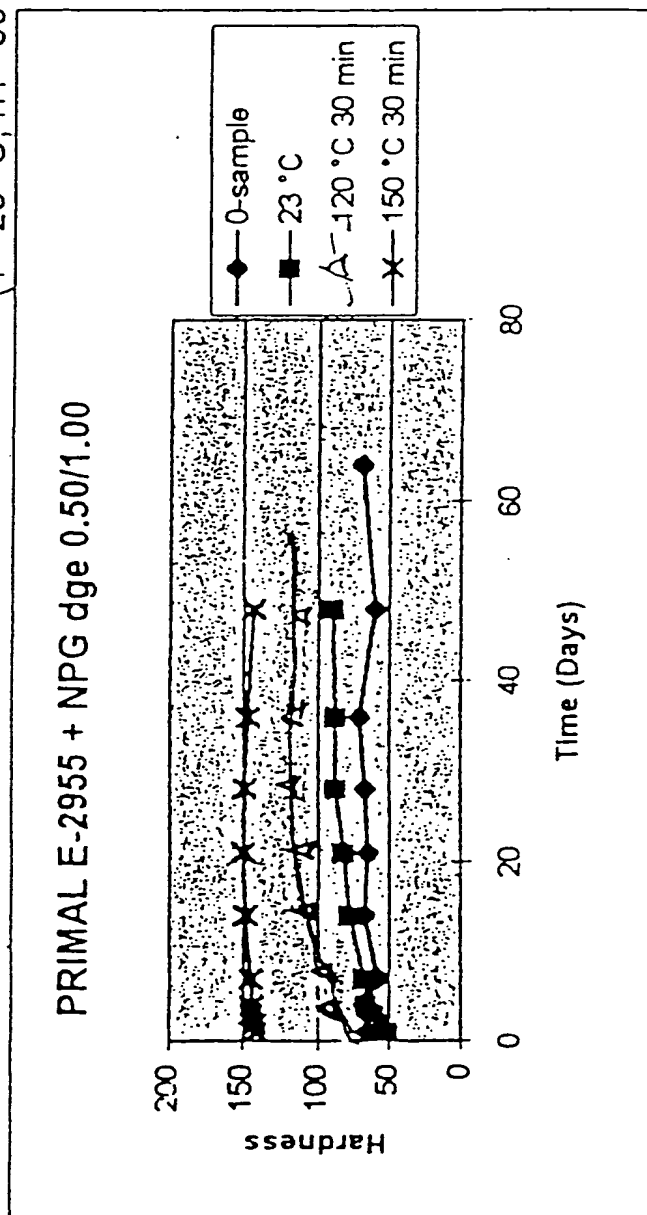
15 14. Method of accelerating the hardening of an aqueous paint composition containing  
binder, coalescent agent and optionally admixtures and auxiliary agents known *per se*,  
c h a r a c t e r i z e d by incorporating into the composition a glycidyl ether or ester or a  
mixture thereof, wherein the hydrocarbyl residue of the alcohol or carboxylic acid,  
20 respectively, of the ether or ester comprises a linear or branched, unsaturated or saturated  
hydrocarbon having 3 to 20 carbon atoms, the proportion of the glycidyl ether and/or ester  
being at least 20 wt.-% of the film forming agents of the paint composition.

15. The method according to claim 14, c h a r a c t e r i z e d by incorporating at least 50  
25 wt.-% of a glycidyl ether and/or ester, whereby the paint composition attains at least 70 %  
of its final hardness within a day.

16. Use of a glycidyl ether or ester as film forming agent in aqueous paint compositions,  
said ether or ester containing a linear or branched, saturated or unsaturated hydrocarbyl  
30 residue having 3 to 20 hydrocarbyl residue with 3 to 20 carbon atoms which is linked to the  
glycidyl group via an ether or ester bond.

1/1

(T = 23 °C, rH = 50 %).



# PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	<b>FOR FURTHER ACTION</b>		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/FI00/00039	International filing date ( <i>day/month/year</i> ) 18.01.2000	Priority date ( <i>day/month/year</i> ) 18.01.1999	
International Patent Classification (IPC) or national classification and IPC <sub>7</sub> C09D 7/00			
Applicant Neste Chemicals OY et al			

<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>5</u> sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of _____ sheets.</p>
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the report</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input checked="" type="checkbox"/> Certain observations on the international application</p>

Date of submission of the demand  10.08.2000	Date of completion of this report  02.05.2001
Name and mailing address of the IPEA/SE Patent- och registreringsverket      Telex Box 5055                                      17978 S-102 42 STOCKHOLM                      PATOREG-S Facsimile No. 08-667 72 88	Authorized officer  Ellen Setréus/Els Telephone No. 08-782 25 00

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI00/00039

**I. Basis of the report****1. With regard to the elements of the international application:\***

- ☒ the international application as originally filed
- ☐ the description:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_
- ☐ the claims:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, as amended (together with any statement) under article 19  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_
- ☐ the drawings:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_
- ☐ the sequence listing part of the description:  
pages \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

**2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.**These elements were available or furnished to this Authority in the following language English which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☒ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

**3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:**

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

**4. ☐ The amendments have resulted in the cancellation of:**

- ☐ the description, pages \_\_\_\_\_
- ☐ the claims, Nos. \_\_\_\_\_
- ☐ the drawings, sheet/fig \_\_\_\_\_

**5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2 (c)).\*\***

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item I and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI00/00039

**Supplemental Box**

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: V

D2 discloses an aqueous resin dispersion that consists of (I) 90-99,8 wt. % aqueous dispersion of a polymer of at least one olefinically unsaturated compound and (II) 0.2-10 wt. % glycidyl ether having epoxide value 0.1-0.8. The resin is prepared by homogeneously mixing (I) and (II). The coatings, which are provided from the resin, have improved wet-adhesion.

The disclosures of D1 differ from the claimed invention in that D1 does not contain a separate glycidyl derivative. Furthermore, the composition of D1 does not contain a binder and a coalescence agent. Thus, the composition of the claimed invention is different from the composition disclosed in D1.

The subject matter of the claimed invention differs from D2 in that at least 20 wt% of the film forming agent is formed by a glycidyl ether. Furthermore, the glycidyl ethers mentioned in D2 are different from the glycidyl ethers disclosed in the claimed invention.

None of the cited documents, taken alone or in combination, reveal the invention defined in claims 1-16. Furthermore, in the cited documents there are no suggestions leading a person skilled in the art towards the invention defined by claims 1-16. The subject matter of claims 1-16 is therefore considered to fulfil the requirements of novelty, inventive step and industrial applicability.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI00/00039

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claim 1 lacks a "wt. %" in the phrase "... at least 20 % of the film forming agent..."



## Maalikoostumukset

Esillä oleva keksintö koskee patenttivaatimuksen 1 johdannon mukaista maalikoostumusta. Tällainen koostumus sisältää yleensä sideainetta, kalvonmuodostusainetta sekä sinänsä tunnettuja lisä- ja apuaineita.

- 5      Keksintö liittyy edelleen patenttivaatimuksen 14 johdannon mukaiseen menetelmään maalikoostumuksen kovettumisen nopeuttamiseksi sekä patenttivaatimuksen 16 mukaiseen käyttöön.

- 10      Monet lateksimaaleissa käytettävät emulsiopolymeerit eivät muodosta kalvoa kohtuullisissa tai alhaisissa lämpötiloissa. Jotta kalvonmuodostuminen olisi näissä olosuhteissa mahdollista, lateksimaleihin lisätään kalvonmuodostusaineita (*coalescent agents*). Liuotinpohjaisissa maaleissa käytettävät liuottimet toimivat kalvonmuodostuslämpötilan alentajana. Kalvonmuodostuskemikaalit ovat usein orgaanisia liuottimia, jotka maalin kuivuessa ja kovettuessa haihtuvat ympäröivään ilmaan aiheuttaen haju- ja saasteongelman.
- 15      Osaltaan perinteiset kalvonmuodostusaineet lisäävät siis haihtuvien komponenttien määrää (*VOC*) ja maalin kokonaisemissioita.

- Kalvonmuodostusaineiden kehittäminen pyrkii tuomaan markkinoille korvaavia kalvonmuodostusaineita, jotka eivät lukeudu haihtuviin orgaanisiin yhdisteisiin (*VOC*-komponentit). Kuitenkin haihtumattomien tai hitaasti haihtuvien komponenttien haittana on niiden tuoma pehmitinominaisuus, jolloin maalikalvon kovuus kehittyy hitaasti ja saattaa jäädä pehmeäksi.
- 20

- Maaliseoksissa, joissa ei haluta ympäristölle haitallisia päästöjä, voidaan käyttää erilaisia reaktiivisia kalvonmuodostusaineita. Näiden yhdisteiden tarkoitus on reagoida osaksi maalikalvoa, jolloin päästöt jäävät mahdollisimman vähäisiksi. Reaktiivisten kalvonmuodostajien tarkoituksena on sekä parantaa kovuuden kehittymistä että alentaa kalvonmuodostuslämpötilaa. Tällaisia yhdisteitä ovat mm. erilaiset isosyanaatit ja epoksidit sekä siloksaanit.
- 25

- 30      Rakenteestaan johtuen reaktiivisten yhdisteiden kalvonmuodostuslämpötilaa alentava

vaikutus on usein hyvin vähäinen verrattuna normaaleihin haihtuviin tai ns. no-VOC kalvonmuodostajiin. Lisäksi isosyanaatit ovat herkkiä kosteudelle eikä niitä siten voida käyttää vesidispersioissa. Jotta päästään maalien käytössä vaadittaviin kalvonmuodostus-  
5 lämpötiloihin, täytyy reaktiivisten yhdisteiden lisäksi käyttää perinteisiä kalvonmuodostajia.

Esillä olevan keksinnön tarkoituksena on poistaa tunnettuun tekniikkaan liittyvät epäkohdat ja saada aikaan aivan uudenlaiset maalikoostumukset.

10 Glysidyyliesterien käyttö liuotepohjaisissa maaleissa on ennestään tunnettua. Niinpä kansainvälisessä hakemusjulkaisussa WO 97/44335 on todettu, että glysidyyliestereitä voidaan käyttää epoksi-, uretaani ja polyesterimaalien valmistuksen reaktiivisena laimentimena. Julkaisussa ei ole mitään mainintaa glysidyyliesterien muista ominaisuuksista, esim. niiden kalvonmuodostuskyvystä.

15 Esillä oleva keksintö perustuu siihen havaintoon, että suurikokoisen hiilivetytähteen sisältävillä glysidyylijohdannaisilla, etenkin glysidyyliettereillä ja glysidyyliestereillä, on erinomaiset kalvonmuodostusominaisuudet ja hyvä dispergoitavuus veteen. Keksinnön mukaan käytetään siksi vesipohjaisten maalikoostumusten kalvonmuodostusaineina glysidolin (2,3-epoksi-1-propanolin) ja 3 - 20 hiiltä sisältävän orgaanisen alkoholin tai  
20 karboksyylihapon muodostamaa eetteriä tai esteriä. Yllättäen on todettu, että tällaisilla yhdisteillä voidaan kokonaan tai osittain korvata maalikoostumusten nykyiset kalvonmuodostajat etenkin niiden reaktiiviset kalvonmuodostajat. Niillä voidaan merkittävästi nopeuttaa maalikalvon kovettumista.

25 Glysidyyliestereitä, kuten 2-etyyliheksanolin glysi-dyyliesteriä, voidaan valmistaa varsin korkealla saannolla ja suurella puhtaudella, vastaa-vista karboksyylihapoista muodostamalla ensin karboksyylihapon alkalimetallisuola, sekoittamalla kyseinen suola yhteen epikloorihydriinin kanssa, jota jälkimmäistä yhdistettä on molaarinen ylimäärä, ja  
30 pitämällä reaktioseos ainakin noin 60 °C:ssa palautusjäähdytyksessä. Reaktiota voidaan jatkaa sanotussa lämpötilassa ilman merkittävää sivutuotteiden muodostumista, kunnes glysidyyliesterin saanto on ainakin 80 %.

35 Täsmällisemmin sanottuna keksinnön mukaiselle maalikoostumukselle on tunnusomaista se, mikä on esitetty patenttivaatimuksen 1 tunnusmerkkiosassa.

Keksinnön mukaiselle menetelmälle maalikoostumuksen kovettumisen nopeuttamiseksi on tunnusomaista se, mikä on esitetty patenttivaatimuksen 14 tunnusmerkkiosassa, ja keksinnön mukaiselle käytölle se, mikä on esitetty patenttivaatimuksen 16 tunnusmerkkiosassa.

5 Keksinnön avulla saavutetaan huomattavia etuja. Niinpä keksinnön mukaisilla kalvonmuodostajilla saadaan aikaan hyvä dispersio maaliseoksissa, mikä näyttää johtuvan heikosti poolisesta eetterisidoksesta tai enemmän poolisesta esterisidoksesta. Lisäksi eetterin tai esterin suurehkon hiilivetyryhmän takia uudet kalvonmuodostajat alentavat paremmin kalvonmuodostuslämpötilaa kuin normaalisti käytössä olevat siloksaanit tai epoksidiyhdisteillä. Yhdisteiden alhaisen haihtuvuuden ansiosta niitä voidaan käyttää ns. no-VOC -sovelluksissa. Lisäksi yhdisteiden sisältämän reaktiivisen glysidyyliryhmän ansiosta kalvonmuodostajat saadaan reagoimaan osaksi maalikalvoa, jolloin kokonaisemissiot pienenevät ja maalikalvon kovuus kehittyy suotuisasti.

15 Yhdisteillä voidaan nopeuttaa kalvon kovettumista siten, että ainakin 70 % lopullisesta kovuudesta saavutetaan jo noin 1 vrk sisällä. Esillä olevia glysidyylieettereitä ja -estereitä voidaan käyttää yhdessä tunnettujen kalvonmuodostajien kanssa.

20 Keksintöä ryhdytään seuraavassa lähemmin tarkastelemaan yksityiskohtaisen selityksen ja muutaman esimerkin avulla.

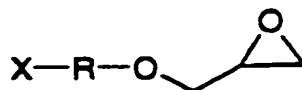
Oheisessa kuviossa on esitetty Primal E- 2955+NPG-diglysidyylieetterin Königheilurikovuuden kehittyminen lasilevyillä ( $t = 23\text{ }^{\circ}\text{C}$ ,  $rh = 50\%$ ) eri lämpötiloissa moolisuhteella epoksi/karboksyylihappo-ryhmät = 0,5/1,0.

25 Esillä olevassa keksinnössä käytetään maalikoostumusten kalvonmuodostusaineina sellaisia glysidyylieettereitä ja/tai estereitä, jotka sisältävät glysidyyliryhmään eetteri- tai esterisidoksen kautta liittyvän, suoran tai haaroittuneen hiilivetytähteen, jossa on 3 - 20, tavallisesti 4 - 18 hiiliatomia, edullisesti 4 - 12 hiiliatomia. Lyhyet hiiliketjut antavat 30 nopeamman kovuuden kehittymisen ja lisäävät kalvon lopullista kovuutta.

Niinpä keksinnössä käytettävissä eettereissä ainakin yksi alkoholitähde on peräisin glysidolista (2,3-epoksi-1-propanolista), joka on muodostanut eetteriryhmän 3 - 20 hiiliatomia sisältävän suoran tai haaroittuneen monoalkoholin, diolin, triolin, tetraolin tai pentolin 35 kanssa.

Edullisten glysidyylietterien rakennetta on kuvattu kaavassa I

5



I

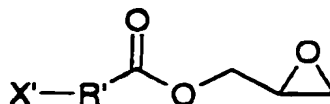
- 10 jossa R on suora tai haaroittunut, tyydyttymätön tai tyydyttynyt C<sub>3</sub>-C<sub>20</sub>-hiilivety, jossa mahdollisesti on yksi tai useampi hydroksyyli-ryhmä, ja  
X edustaa vetyä tai hydroksyyli-ryhmää.

15 Eetterijohdannaisessa voi olla 1, 2, 3, 4 tai 5 glysidyylietteriryhmää. Glysidyylietteri-ryhmiä voi myös sisältyä hydroksi- haposta johdettuihin glysidyyli-estereihin. Di- ja poly-oleista peräisin olevissa glysidyylietteriyhdisteissä voi myös olla muista alkoholeista johdettuja eetteriryhmiä (sekaeetterit). Etenkin nämä toiset alkoholit ovat alkanoleja, kuten  
20 alempia alkanoleja (metanoli, etanoli, propanolit, butanolit). Muista alkoholeista peräisin olevat eetteriryhmät, mikäli näitä yhdisteessä on läsnä, muodostavat yleensä korkeintaan 80 mooli-%, edullisesti 1 - 50 mooli-% eetteripohjaisten kalvonmuodostajien eetteriryhmistä.

Esillä olevien kalvonmuodostajien toisen pääryhmän muodostavat esterit, joissa alkoholi-  
tähde on peräisin glysidolista ja karboksyyli- hapon tähde on peräisin 3 - 20, edullisesti 4 -  
18, erityisen edullisesti 4 - 12 hiiliatomia sisältävästä suorasta tai haaroittuneesta yksi- tai  
25 useampi- protonisesta karboksyyli- haposta (eli haposta, joka sisältää useamman karboksyyli-ryhmän). Useampi- protonisista hapoista saadaan mono-, di-, tri- jne. estereitä. Esterit voivat olla puoli-estereitä tai täy-estereitä.

Edullisten glysidyyliesterien rakennetta on kuvattu kaavassa II

30



II

- 35 jossa R' on suora tai haaroittunut, tyydyttymätön tai tyydyttynyt C<sub>2</sub>-C<sub>20</sub>-hiilivety, jossa mahdollisesti on yksi tai useampi hydroksyyli-ryhmä, ja

X' edustaa metyyliryhmää, metyleenihydroksiryhmää tai karboksyyli- tai alempaa karboksylaattiryhmää.

5 Alemmista karboksylaattiryhmistä mainittakoon etenkin metoksylaatti (–COOMe) ja etoksilaatti (–COOEt).

10 Esterit myös valmistaa hydroksihapoista, kuten edellä mainittiin, jolloin niissä voi olla eetteriryhmiä. Useampiemäksisten happojen glysidyyliestereihin voi sisältyä glysidolin lisäksi muista alkoholeista johdettuja esteriryhmiä (sekaesterit). Kuten yllä mainittiin eetterien kohdalla, nämä toiset alkoholit ovat etenkin alkanoleja, kuten alempia alkanoleja, esim. metanoli, etanoli, propanolit tai butanolit.

15 Esimerkkeinä monoalkoholeista johdetuista eettereistä mainittakoon 2-etyyliheksyyli-glysidyylietteri ja oktyyliglysidyylietteri. Dialkoholista johdettuja eettereitä edustavat neopentyyliglykolin mono- ja dieetterit ja trieettereistä mainittakoon trimetanolipropaanin triglysidyylietteri.

20 Glysidyyliestereistä voidaan mainita 2-etyyliheksyyliglysidyyliesteri, oktyyliglysidyyliesteri ja isopentyyliglysidyyliesteri sekä sekaestereistä glutaarihapon metyyliglysidyyliesteri.

25 Glysidyylietterit voidaan valmistaa Williamsonin eetterisynteesillä epikloorihydriinistä ja alkoholista. Glysidyylietterien valmistusta on kuvattu artikkelissa Kida, T., Yokota, M., Masuyama, A. ja Okahara, M., Synthesis 1993, 487-489. Koska epikloorihydriinin ja hydroksyyli-ryhmän välisestä reaktiosta vapautuu vetykloridia, eetteröinti suoritetaan edullisesti emäksisessä väliaineessa, joka kykenee sitomaan vetykloridin. Alla esitetyissä esimerkeissä on käytetty kaliumhydroksidipitoista väliainetta, jolloin vetykloridista saadaan kaliumkloridia, joka on erotettavissa reaktiojärjestelmästä suodattamalla. Orgaanisen faasin liuottimena reaktiojärjestelmässä voidaan käyttää aromaattista liuotinta, kuten tolueenia, DMSO:ta tai jotain eetteriä, kuten THF:ää.

30 Eetteröinti suoritetaan sopivimmin normaali-ilmanpaineessa ja noin 0...80 °C:n lämpötilassa. Edullisesti reaktio suoritetaan huoneenlämpötilaa korkeammassa lämpötilassa (yli 25 °C:ssa) ja lämpötilaa nostetaan reaktanttien lisäyksen jälkeen reaktion nopeuttamiseksi. Tuote otetaan talteen orgaanisesta faasista uuttamalla ja alipainetislaamalla.

35 Epikloorihydriiniä käytetään ylimäärin suhteessa hydroksyyli-ryhmiin. Epikloorihydriinin ja

alkoholin hydroksyyliyhien moolisuhde on 10:1 - 1:1, edullisesti 5:1 - 2:1.

Keksinnön kannalta sopivia alkoholeja reagoivien alkoksidiien valmistamiseksi ovat jäljempänä luetellut monoalkoholit sekä diolit ja triolit. Tarkoitukseen sopivia alkoholeja ovat yleisesti 3 - 20 (etenkin 4-18, edullisesti 4 - 12) hiiliatomia sisältävät haaroittuneet tai suoraketjuiset monoalkoholit, diolit ja triolit. Erityisesti sopivia alkoholeja maaliseoksissa käytettäviksi glysidyyliesterien lähtöaineiksi ovat mm. 1-butanoli, 2-butanoli, isobutanoli, 1-pentanol, isopentanol, 1-heksanol, 2-etyyliheksanol, 1-heptanol, 1-oktanol, 2-etyyli-1,3-heksaani-dioli, neopentyyliglykoli, 2-butyli-2-etyyli-1,3-propaanidioli, trimetylietaani ja trimetyl-olipropaani. Muita sopivia alkoholeja ovat 1,4-butaanidioli, neodekaanialkohol, 1,6-heksaanidioli, 1,10-dekaanidioli ja 2-etyyli-2-heksen-1-oli.

Keksinnön mukaisia glysidyyliesteriä voidaan valmistaa epikloorihydriinistä ja hapoista ja niiden johdannaisista esim. vaihtoesteröinnillä saattamalla karboksyylihappojen alkalimetallisuola, esim. natriumsuola, reagoimaan epikloorihydriinin kanssa. Dikarboksyylihapoista voidaan happojen lisäksi lähtöaineena käyttää vastaavaa anhydridiä, josta muodostetaan sopiva alkalimetallisuola. Karboksyylihappojen glysidyyliesterien valmistusta on kuvattu artikkelissa Kester, E.B., Gaiser, C.J. ja Lazar, M.E., J. Org. Chem., 8 (1943) 550 ja anhydridien alkyli-glysidyyliesterien valmistusta artikkelissa Zlatanov, S.N. ja Sagredos, A.N., JAOCS, 67 (1990) 661.

Esterit voidaan myös valmistaa suoralla esteröinnillä.

Varsinaisen esteröintireaktion lämpötila on 30 - 120 °C, sopivimmin noin 50 - 100 °C. Reaktio suoritetaan normaali-ilmanpaineessa. Esteröinnissä voidaan käyttää katalyyttiä noin 1 - 40 % esteröintiaineen määrästä. Sopivia esteröintikatalyytteja ovat p-tolueenisulfoni-happo, bentseenisulfoni-happo, rikkihappo, tina- ja sinkkisuolat tai -oksidit sekä titanaatit. Sopivia vaihtoesteröintikatalyyttejä taas ovat alkalimetallialkoksidit, esim. kalium- tai natriumalkoksidit, rikkihappo, suolahappo ja happamat ioninvaihtohartsit.

Edullisen sovellutusmuodon mukaan esteröinti suoritetaan muodostamalla 3 - 20 hiiliatomia sisältävästä, lineaarisesta tai haarautuneesta, tyydyttymättömästä tai tyydyttyneestä karboksyylihaposta ensin sen alkalimetallisuola. Karboksyylihapon alkalimetallisuolasta ja epikloorihydriinin molaarisesta ylimäärästä muodostetaan sitten reaktioseos, joka pidetään ainakin noin 60 °C:ssa palautusjäähdyksessä. Koska reaktioseoksessa on useita komponentteja, reaktiolämpötila voi vaihdella palautusjäähdytyksen

- olosuhteissa jopa 20 - 50 aseteella. Tavallinen lämpötila-alue reaktion aikana on noin 65 - 100 °C. Reaktiota jatketaan tämän jälkeen ainakin 1 tunnin ajan sanotussa lämpötilassa, kunnes glysidyyliesterin saanto on ainakin 80 %, tyypillisesti ainakin 90 %. Sivutuotteiden muodostus on alle 5 % lopputuotteesta, ja tuotteen puhtaus onkin yli 95 %. Reaktiossa
- 5 epikloorihydriinin ylimäärä on ainakin 50 %, tyypillisesti epikloorihydriinin moolisuhde reagoivan karboksyylihapon karboksyyliiryhmiin nähden on 2-...5-kertainen. Yllättäen on todettu, että esim. 2-etyyliheksaanihaposta voidaan valmistaa sen glysidyyliesteri varsin korkealla, tyypillisesti yli 90 %:n, saannolla ja erittäin puhtaana (puhtaus yli 95 %).
- 10 Esteröintiin sopivia happoja ovat yleisesti 4-18 hiiliatomia sisältävät haaroittuneet tai suoraketjuiset mono- tai dikarboksyylihapot sekä hydroksihapot. Erityisen sopivia happoja maalisokseissa käytettävien glysidyyliesterien lähtöaineiksi ovat mm. butaanihappo, iso-
- butaanihappo, pentaanihappo, isopentaanihappo, 1-heksaanihappo, 2-etyyliheksaanihappo, heptaanihappo, oktaanihappo, neodekaanihappo, 2-hydroksi-isobutaanihappo, 2,2-di-
- 15 metyyli-3-hydroksi-propaanihappo, adipiinihappo, fumaarihappo sekä maleiinihappo, meripihkahappo, glutaarihappo ja näiden anhydridit sekä muut johdannaiset sekä 2-etyyli-2-hekseenihappo, öljyhappo ja linolihappo.
- Keksinnön mukaisia glysidyylietteereitä ja glysidyyliestereitä voidaan formuloida vesi-
- 20 pohjaisiksi dispersioiksi, jotka sisältävät veteen dispergoituvaa sideainetta ja sinänsä tunnettuja lisä- ja apuaineita. Sideaineina voivat toimia mm. lateksimaalien sideaineet, kuten polyvinyylasetaatit ja polyakrylaatit. Yleisesti polyakrylaatit käsittävät synteettisen lateksin, joka on etyleenisesti tyydyttymätön polymeeri tai komonomeeri, kuten akryyli-
- happo, itakonihappo tai maleiinihappo. Polyvinyyli-asetaatissa voi olla karboksyyliiryhmiä
- 25 sisältäviä komonomeerejä. Muita veteen dispergoitavia sideaineita ovat erilaiset vesiliukoiset polymeerit (esim. PVA), tärkkelys, CMC, hydroksietyyli-selluloosa ja polyvinyyli-alkoholi.
- Edellisten lisäksi sideaineina voidaan käyttää veteen dispergoituva alkydeja. Nämä
- 30 käsittävät tavallisesti kaksi-arvoisesta polyolista ja rasvahaposta tai luonnonöljystä muodostetun kondensaattituotteen. Jotta ne dispergoituisivat tai jopa osittain liukenisivat helpommin veteen, niissä on tyypillisesti karboksyylihapporyhmiä.
- Erityisen edullista on käyttää keksinnön mukaisia glysidyylietteereitä ja/tai estereitä
- 35 maalikoostumuksissa, joissa on sideaine, joka muodostaa kovan kalvon maalin kuiyuttua. Sopivia sideaineita ovat esim. akrylaattilateksit, joissa styreeni on polymeroitu yhden tai

useamman akrylaatti- tai metakrylaattimonomeerin kanssa. Tällaisia latekseja edustavat karboksifunktionaaliset styreeni-akrylaatti-lateksit, kuten styreeni-metyylimetakrylaatti- tai styreeni-butyliakrylaatti-lateksit. Alla esitetyssä esimerkissä 11 on kuvattu keksinnön mukaisten kalvonmuodostajien käyttöä yhdessä styreeni-etyylialkrylaatin ja styreeni-2-ethyyliheksyyliakrylaatti-metyylimetakrylaatin kanssa. Muista sopivista latekseista mainittakoon styreeni-2-etyyliheksyyliakrylaatti-vinyylisetaatti ja styreeni-2-etyyliheksyyliakrylaatti-metyylimetakrylaatti-n-butyliakrylaatti.

Sideaineen määrä on tavallisesti 20 - 80 % dispersiosta. Himmeissä katto- ja seinämaaleissa, kuten myös vesiohenteisissa korroosionestomaaleissa, voidaan kuitenkin käyttää tätä pienempiäkin määriä. Tyypillisissä kaupallisissa latekseissa varsinaisen polymeerin määrä on näet noin 30 - 60 %, etenkin noin 50 %. Koska maaleissa voi olla jopa vain 10 % lateksia, niin himmeissä maaleissa on vain noin 5 % polymeeristä sideainetta. Niinpä yleisesti keksinnön mukaisissa maalikoostumuksissa sideainetta on 3 - 80 %, etenkin 4 - 60 %.

Dispersioiden lisä- ja apuaineista mainittakoon pinta-aktiiviset aineet, dispergointiaineet, sakeuttamisaineet, säilöntä-aineet/fungisidit, vaahdonestoaineet sekä täyteaineet ja pigmentit, esim. kalsiumkarbonaatti ja titaanidioksidi, ja pH:n säätöaineet, kuten ammoniakkin vesiliuos.

Keksinnön mukaisten reaktiivisten kalvonmuodostusaineiden määrä dispersiosta on noin 0.01 - 20 paino-%, edullisesti 0.1 - 15 paino-%. Maalikoostumuksen kalvonmuodostaja voi koostua pelkästään glysidyyliettereistä, glysidyyliestereistä tai niiden seoksista tai etterien ja/tai esterien ja tavanomaisten kalvonmuodostusaineiden seoksesta. Yleensä glysidyylietterien tai -esterien osuus kalvonmuodostusaineiden kokonaismäärästä on ainakin 20 paino-%, tyypillisesti yli 50 %. Edullisesti esillä olevia glysidyylijohdannaisia käytetään yhdessä sellaisten kalvonmuodostajien tai kalvonmuodostajien seosten kanssa, joiden kiehumispiste normaali-ilmanpaineessa on ainakin 250 °C. Tällaisia tavanomaisia kalvonmuodostajia ovat esim. etyleeniglykolin fenyylietterit, 2,2,4-trimetyyli-1,3-pentaanidiolin monoisobutyraatti (kauppanimeltään esim. Texanol), dietyleeniglykolin n-butylietteriasetaatti sekä dipropyleeniglykolin mono-n-butylietteri ja tripropyleeniglykolin mono-n-butylietteri (kauppanimeltään Dowanol DpnB ja vastaavasti Dowanol TPnB).

Yksinään tai yhdessä tunnettujen kalvonmuodostajien kanssa esillä olevat glysidyylijohdannaiset kykenevät merkittävästi nopeuttamaan maalikoostumusten kovuuden kehiti-



tymistä. Lopulliseen kovuuteen päästään jo 7 - 14 vuorokaudessa, jolloin ainakin 70 %, etenkin ainakin 80 % ja tavallisesti ainakin 90 %, kalvon lopullisesta kovuudesta saavutetaan 24 tunnin sisällä, kun koostumuksen kalvonmuodostajista ainakin 20 %, edullisesti ainakin 50 % koostuu glysidyylijohdannaisista.

5

Esillä olevien reaktiivisten kalvonmuodostajien stabiilisuuden ja maalikoostumusten käytön kannalta on edullista, että maalikoostumusten pH-arvo on neutraali tai hapan, etenkin neutraali tai lievästi hapan. Sopivimmin maalikoostumusten pH on pienempi kuin noin 8,5, edullisesti se on alle 8,0.

10

Esillä olevia kalvonmuodostusaineita on verrattu kaupallisiin tuotteisiin. Esimerkkien 4, 5 ja 9 glysidyyliyhdisteet toimivat maaliseoksissa kalvonmuodostuslämpötilaa alentavasti ja paremmin kuin vertailtava kaupallinen yhdiste (Coatosil 1770). Taulukoista 1 ja 2 voidaan todeta, että useiden valmistettujen glysidyyliyhdisteiden kiehumispisteet ovat yli 250 asteen ja niiden haihtumisnopeudet ovat alhaisia, jolloin niiden käyttö alhaisen haihtuvuuden vuoksi on turvallisempaa kuin perinteisten reaktiivisten monomeerien. Kaikkien testattujen glysidyyliyhdisteiden kanssa maalikalvojen kovuus kehittyy suotuisasti. Esimerkissä 11 on tarkasteltu Primal E- 2955+NPG-diglysidyylietterin König-kovuuden kehittymistä lasi-levyillä eri lämpötiloissa moolisuhteella epoksi/karboksyylihappo-ryhmät 0,5/1,0. Kaikissa lämpötiloissa kovuus kehittyi paremmin kuin 0-näytteillä.

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Seuraavat ei-rajoittavat esimerkit havainnollistavat keksintöä:

### **Esimerkki 1**

25

#### *2-Etyyliheksanolin glysidyylietterin valmistus*

2-Etyyliheksanolin (1 mooliekvivalentti) ja kaliumhydroksidin (2 mol-eq) liuokseen DMSO:ssa lisätään hitaasti epikloorihydriiniä (3 mol-eq). Seosta lämmitetään epikloorihydriinin lisäyksen aikana n. 35 °C:ssa ja lisäyksen jälkeen 45 °C:ssa. Syntynyt KCl-suola suodatetaan ja orgaaninen faasi uutetaan eetteriin. Kuivatuksen jälkeen tuote tislataan alipaineessa. Tuotteen puhtaus 97 % ja saanto tislauksen jälkeen 50 % teoreettisesta.

30

**Esimerkki 2***1-Oktanolin glysidyylietterin valmistus*

1-Oktanolin (1 mooliekvivalentti) ja kaliumhydroksidin (2 mol-eq) liuokseen DMSO:ssa  
 5 lisätään hitaasti epikloorihydriiniä (3 mol-eq). Seosta lämmitetään epikloorihydriinin  
 lisäyksen aikana n. 35 °C:ssa ja lisäyksen jälkeen 45 °C:ssa. Syntynyt KCl-suola  
 suodatetaan ja orgaaninen faasi uutetaan eetteriin. Kuivauksen jälkeen tuote tislataan  
 alipaineessa. Tuotteen puhtaus 100 % ja saanto tislauksen jälkeen 32 % teoreettisesta.

**Esimerkki 3***Isobutanolin glysidyylietterin valmistus*

Isobutanolin (1 mooliekvivalentti) ja kaliumhydroksidin (2 mol-eq) liuokseen DMSO:ssa  
 lisätään hitaasti epikloorihydriiniä (3 mol-eq). Seosta lämmitetään epikloorihydriinin  
 15 lisäyksen aikana n. 35 °C:ssa ja lisäyksen jälkeen 45 °C:ssa. Syntynyt KCl-suola  
 suodatetaan ja orgaaninen faasi uutetaan eetteriin. Kuivatuksen jälkeen tuote tislataan  
 alipaineessa. Tuotteen puhtaus 94 % ja saanto tislauksen jälkeen 17 % teoreettisesta.

**Esimerkki 4****20** *Neopentyyliglykolin diglysidyylietterin valmistus*

Neopentyyliglykolin (1 mooliekvivalentti) ja kaliumhydroksidin (2 mol-eq) liuokseen  
 DMSO:ssa lisätään hitaasti epikloorihydriiniä (3 mol-eq). Seosta lämmitetään  
 epikloorihydriinin lisäyksen aikana n. 35 °C:ssa ja lisäyksen jälkeen 45 °C:ssa. Syntynyt  
 25 KCl-suola suodatetaan ja orgaaninen faasi uutetaan eetteriin. Kuivauksen jälkeen tuote  
 tislataan alipaineessa. Tuotteen puhtaus 97 % ja saanto tislauksen jälkeen 50 %  
 teoreettisesta.

**Taulukko 1.** Esimerkeissä 1-4 valmistettujen glysidyylietterien ominaisuuksia.

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Nimi	kp (°C)	haihtumisnop. (ButAc = 1)
Esimerkki 1. 2-etyyliheksyyli glysidyylietteri	221	0.005110
Esimerkki 2. oktyyli glysidyylietteri	255	-
Esimerkki 3. isobutyli glysidyylietteri	168	-
35 Esimerkki 4. neopentyyli glykolin diglysidyyli- etteri	275	0.000387

**Esimerkki 5***2-Etyyliheksyylihapon glysidyyliesteri*

- 5 2-Etyyliheksaanihappoa 1 mol-ekv. ja NaOH 2 mol-ekv. toluenissa valmistetaan hapon Na-suola. Toluenin avulla poistetaan syntyvä vesi atseotrooppisella tislauksella. Tämän jälkeen reaktioseos jäädytetään 50 °C:een ja lisätään hitaasti 3 mol-ekv. epikloorihydriiniä. Epikloorihydriinin lisäyksen jälkeen seosta refluksoidaan 1-8 h 65...100 °C:ssa. Epikloorihydriini poistetaan tislamalla ja tuote tislataan alipaineessa. Tuotteen  
10 saanto reaktion jälkeen 94 % ja tislatus tuotteen puhtaus 98 %.

**Esimerkki 6***Oktaanihapon glysidyyliesteri*

- 15 Oktaanihappoa 1 mol-ekv. ja NaOH 2 mol-ekv. toluenissa valmistetaan hapon Na-suola. Toluenin avulla poistetaan syntyvä vesi atseotrooppisella tislauksella. Tämän jälkeen reaktioseos jäädytetään 50 °C:een ja lisätään hitaasti 3 mol-ekv. epikloorihydriiniä. Epikloorihydriinin lisäyksen jälkeen seosta refluksoidaan 1-8 h 65...100 °C:ssa. Epikloorihydriini poistetaan tislamalla ja tuote tislataan alipaineessa. Tuotteen saanto  
20 reaktion jälkeen 24 % ja tislatus tuotteen puhtaus 90 %.

**Esimerkki 7***Isobutaanihapon glysidyyliesteri*

- 25 Isobutaanihappoa 1 mol-ekv. ja NaOH 2 mol-ekv. toluenissa valmistetaan hapon Na-suola. Toluenin avulla poistetaan syntyvä vesi atseotrooppisella tislauksella. Tämän jälkeen reaktioseos jäädytetään 50 °C:een ja lisätään hitaasti 3 mol-ekv. epikloori-hydriiniä. Epikloorihydriinin lisäyksen jälkeen seosta refluksoidaan 1-8 h 65...100 °C:ssa. Epikloorihydriini poistetaan tislamalla ja tuote tislataan alipaineessa. Tuotteen saanto  
30 reaktion jälkeen 65 % ja tislatus tuotteen puhtaus 100 %.

**Esimerkki 8***2,2-dimetyyli-3-hydroksipropaanihapon glysidyyliesteri*

- 35 2,2-dimetyyli-3-hydroksipropaanihappoa 1 mol-ekv. ja NaOH 2 mol-ekv. toluenissa valmistetaan hapon Na-suola. Toluenin avulla poistetaan syntyvä vesi atseotrooppisella

tislauksella. Tämän jälkeen reaktioseos jäädytetään 50 °C:een ja lisätään hitaasti 3 mol-ekv. epikloorihydriiniä. Epikloorihydriinin lisäyksen jälkeen seosta refluksoidaan 1-8 h 65-100 °C:ssa. Epikloorihydriini poistetaan tislamalla ja tuote tislataan alipaineessa. Tuotteen saanto reaktion jälkeen 45 % ja tislatus tuotteen puhtaus 87 %.

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**Esimerkki 9***Glutaarihapon metyyli-glysidyyliesteri*

Glutaarihapon anhydridiä 1 mol-ekv. lisätään 1 normaalseen NaOH/metanoli/tolueeniliuokseen. Seos jäädytetään ja ylimääräinen metanoli tislataan pois. Saatu glutaarihapon metyyliesterin Na-suola uudelleenkiteytetään asetonista ja kuivataan. Glutaarihapon Na-suolaa 1 mol-ekv. ja epikloorihydriiniä sekoitetaan ja refluksoidaan 1-3 h 100-115 °C:ssa. Katalyyttinä voidaan käyttää tertaetyyliammoniumjodidia 0.02-0.1 mol-ekv. Na-suolan määrästä. Tuoteseos jäädytetään, suodatetaan ja ylimääräinen epikloorihydriini tislataan pois. Jäänyt seos uutetaan eetteriin ja tislataan vakuuissa. Tuotteen saanto 72 % ja puhtaus 89 %.

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**Esimerkki 10***Isopentaanihapon glysidyyliesteri*

20

Isopentaanihappoa (1 mol-ekv.) ja NaOH (2 mol-ekv.) tolueenissa valmistetaan hapon Na-suola. Tolueenin avulla poistetaan syntyvä vesi atseotrooppisella tislauksella. Tämän jälkeen reaktioseos jäädytetään 50 °C:een ja lisätään hitaasti 3 mol-ekv. epikloorihydriiniä. Epikloorihydriinin lisäyksen jälkeen seosta refluksoidaan 1-8 h 65...100 °C:ssa. Epikloorihydriini poistetaan tislamalla ja tuote tislataan alipaineessa. Tuotteen saanto reaktion jälkeen on 77 % ja tislatus tuotteen puhtaus 96 %.

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Isopentaanihapon glysidyyliesterin kp. on 226-227 °C.

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**Taulukko 2.** Esimerkkien 5-9 glysidyyliesterien ominaisuuksia.

	Nimi	kp (°C)	haihtumisnop. (ButAc = 1)
	Esimerkki 5. 2-etyyliheksyyli glysidyyliesteri	242-246	0.001984
5	Esimerkki 6. Oktyyli glysidyyliesteri	190	-
	Esimerkki 7. Isobutyli glysidyyliesteri	69-71 / 0.1 mmHg	-
	Esimerkki 8. 2,2,dimetyyli-3-hydroksi propaani- hapon glysidyyliesteri	-	-
10	Esimerkki 9. Glutaarihapon metyyli glysidyyli- esteri	282-283	0.000067

**Esimerkki 11**

15 *Valmistettujen glysidyyliyhdisteiden käyttö kalvonmuodostajana vesiliukoisissa  
maalikoostumuksissa.*

Joitain esimerkeissä 1-9 valmistettujen kalvonmuodostajien toimivuutta maaliseoksissa  
testattiin valmistamalla kahdesta eri kaupallisesta lateksidispersiosta (Joncryl 95 ja Primal  
E-2955) seoksia, joihin oli sekoitettu eri pitoisuuksia glysidyyliyhdisteitä. Vertailu-  
20 näytteenä käytettiin kaupallista kalvonmuodostajaa: epoksisiloksaania (Coatosil 1770).  
Vaikutus kalvonmuodostuslämpötilaan selviää oheisesta taulukosta.

**Taulukko 3.** Esimerkeissä 4, 5 ja 9 valmistettujen glysidyyliyhdisteiden vaikutus kalvonmuodostuslämpötilaan Joncryl-95® ja Primal E-2955® latekseilla verrattuna kaupalliseen reaktiiviseen kalvonmuodostajaan (Coatosil 1770) (Joncryl 95 MFFT = 16 °C, kuiva-ainepitoisuus 30 %, Primal E-2995 MFFT = 56 °C\*, kuiva-ainepitoisuus 37 %)

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	Joncryl-95 0%	Joncryl-95 3%	Joncryl-95 6%	Primal- 2955 0%	Primal- 2955 3%	Primal- 2955 6%	Primal- 2955 10%
Esimerkki 4. NPG:n diglysidyyli- eetteri	16	14	0	40	36	24	15
Esimerkki 5. 2-EHA glysidyyli- esteri	16	10	0	40	32	19	11
Esimerkki 9. GA:n met.glysidyyli- esteri	16	14	0	40	37	28	16
Vertailunäyte: Coatosil 1770	16	14	10	40	39	33	29

20

\* Valmistajan ilmoittama arvo kuivalle lateksille

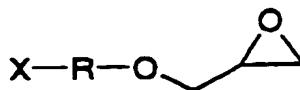
25

Oheisesta kuviosta käy ilmi, miten Primal E-2955+NPG-dge-näytteen König-kovuus on kehittynyt eri lämpötiloissa. Kuten kuviosta näkyy, kovuus on keksinnön mukaisella näytteellä jopa kolminkertainen verrattuna 0-näytteen kovuuteen.

**Patenttivaatimukset:**

1. Vesipohjainen maalikoostumus, joka käsittää sideaineen, kalvonmuodostusaineen sekä mahdollisesti sinänsä tunnettuja lisä- ja apuaineita, t u n n e t t u siitä, että kalvon-
- 5 muodostusaineesta ainakin 20 % koostuu glysidyylietteristä tai -esteristä tai näiden seoksesta, jossa eetterissä tai esterissä alkoholin tai vastaavasti karboksyylihapon hiilivetytähde koostuu 3 - 20 hiiliatomia sisältävästä, lineaarisesta tai haarautuneesta, tyydyttymättömästä tai tyydyttyneestä hiilivedystä.
- 10 2. Patenttivaatimuksen 1 mukainen maalikoostumus, t u n n e t t u siitä, että se sisältää 0,01 - 20 paino-% glysidyylietteriä ja/tai esteriä koostumuksen kuiva-ainepitoisuudesta.
3. Patenttivaatimuksen 1 tai 2 mukainen maalikoostumus, t u n n e t t u siitä, että se sisältää 3 - 80 paino-%, etenkin 4 - 60 paino-% veteen dispergoituvaa sideainetta.
- 15 4. Patenttivaatimuksen 3 mukainen maalikoostumus, t u n n e t t u siitä, että sideaine on polyvinyyliasetaatti, polyakrylaatti, polyvinyylialkoholi, tärkkelys, karboksimeytyyli-selluloosa, hydroksietyyliselluloosa tai alkydi.
- 20 5. Patenttivaatimuksen 4 mukainen maalikoostumus, t u n n e t t u siitä, että sideaine muodostaa kovan polymeerikalvon koostumuksen kuivuttua.
6. Jonkin patenttivaatimuksen 1 - 5 mukainen maalikoostumus, t u n n e t t u siitä, että se sisältää kalvonmuodostajana kaavan I mukaista glysidyylietteriä,

25



I

- 30 jossa R on suora tai haaroittunut, tyydyttymätön tai tyydyttynyt C<sub>3</sub>-C<sub>20</sub>-hiilivety, jossa mahdollisesti on yksi tai useampi hydroksyyli-ryhmä, ja
- X edustaa vetyä tai hydroksyyli-ryhmää.

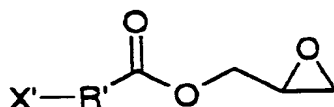
7. Jonkin edellisen patenttivaatimuksen mukainen maalikoostumus, t u n n e t t u siitä, että
- 35 glysidyylietterin hiilivetytähde on johdettu 1-butanolista, 2-butanolista, isobutanolista, 1-pentanolista, isopentanolista, 1-heksanolista, 2-etyyliheksanolista, 1-heptanolista, 1-

oktanolista, 2-etyyli-1,3-heksaanidiolista, neopentyyliglykolista, 2-butyli-2-etyyli-1,3-propaanidiolista, trimetylietaanista, trimetylipropaanista, 1,4-butaanidiolista, neodekaanialkoholista, 1,6-heksaanidiolista, 1,10-dekaanidiolista tai 2-etyyli-2-heksen-1-olista.

5

8. Jonkin patenttivaatimuksen 1 - 4 mukainen maalikoostumus, t u n n e t t u siitä, että se sisältää kalvonmuodostajana kaavan II mukaista glysidyyliesteriä

10



II

jossa R' on suora tai haaroittunut, tyydyttymätön tai tyydyttynyt C<sub>2</sub>-C<sub>20</sub>-hiilivety, jossa mahdollisesti on yksi tai useampi hydroksyyli-ryhmä, ja

15

X' edustaa metyyli-ryhmää, metyleeni- hydroksi-ryhmää tai karboksyyli- tai alempaa karboksylaatti-ryhmää.

9. Jonkin patenttivaatimuksen 1 - 5 tai 8 mukainen maalikoostumus, t u n n e t t u siitä, että glysidyyliesterin karboksyyli-happotähde on johdettu butaanihaposta, isobutaanihaposta, pentaanihaposta, isopentaanihaposta, 1-heksaanihaposta, 2-etyyliheksaanihaposta, heptaanihaposta, oktaanihaposta, neodekaanihaposta, 2-hydroksi-isobutaanihaposta, 2,2-dimetyyli-3-hydroksipropaanihaposta, 2-etyyli-2-hekseenihaposta, öljyhaposta, linolihaposta, adipiinihaposta, fumaarihaposta, maleiinihaposta, meripihkahaposta, glutaarihaposta tai näiden anhydridistä tai muusta johdannaisesta.

25

10. Jonkin edellisen patenttivaatimuksen mukainen maalikoostumus, t u n n e t t u siitä, että kalvonmuodostusaine on 2-etyyliheksyyli- glysidyyli-etteri, oktyyli- glysidyyli-etteri, neopentyyliglykolin mono- tai dieetteri tai trimetanoli- propaanin triglysidyyli-etteri, tai 2-etyyliheksyyli- glysidyyli-esteri, oktyyli- glysidyyli-esteri tai isopentyyli- glysidyyli-esteri tai glutaari- hapon metyyli- glysidyyli-esteri.

30

11. Jonkin edellisen patenttivaatimuksen mukainen maalikoostumus, t u n n e t t u siitä, että sen pH-arvo on pienempi kuin noin 8,5, edullisesti alle 8,0.

35

12. Jonkin edellisen patenttivaatimuksen mukainen maalikoostumus, t u n n e t t u siitä, että se sisältää glysidyyli-etterin ja/tai -esterin lisäksi ainakin yhden toisen kalvonmuodos-



tusaineen, jolloin glysidyylietteri ja/tai -esterin osuus koostumuksen kalvonmuodostus-  
aineista on ainakin 20 p-%, edullisesti ainakin 50 p-%.

5 13. Patenttivaatimuksen 12 mukainen maalikoostumus, t u n n e t t u siitä, että toinen  
kalvonmuodostaja on etyleeniglykolin fenyylietteri, 2,2,4-trimetyyli-1,3-pentaanidiolin  
monoisobutyraatti ja/tai dietyleeniglykolin n-butylietteriasetaatti

10 14. Menetelmä sideainetta, kalvonmuodostusainetta sekä mahdollisesti sinänsä tunnettuja  
lisä- ja apuaineita sisältävän vesipohjaisen maalikoostumuksen kovettumisen nopeutta-  
miseksi, t u n n e t t u siitä, että koostumukseen sisällytetään glysidyylietteri tai -esteri tai  
näiden seos, jossa eetterissä tai esterissä alkoholin tai vastaavasti karboksyylihapon  
hiilivetytähde koostuu 3 - 20 hiiliatomia sisältävästä, lineaarisesta tai haarauneesta,  
tydyttymättömästä tai tyydyttyneestä hiilivedystä, jolloin glysidyylietterin ja/tai esterin  
osuus maalikoostumuksen kalvonmuodostusaineesta on ainakin 20 paino-%.

15 15. Patenttivaatimuksen 14 mukainen menetelmä, t u n n e t t u siitä, että maalikoostumuk-  
seen sisällytetään ainakin 50 paino-% glysidyylietteriä ja/tai esterä, jolloin maalikoostu-  
mus saavuttaa ainakin 70 % lopullisesta kovuudestaan 1 vrk sisällä.

20 16. Sellaisten glysidyylietterien ja -esterien käyttö vesipohjaisten maalikoostumusten  
kalvonmuodostusaineina, jotka sisältävät glysidyyli ryhmään eetteri- tai esterisidoksen  
kautta liittyvän, suoran tai haaroittuneen, tyydyttymättömän tai tyydyttyneen  
hiilivetytähteen, jossa on 3 - 20 hiiliatomia.

## (57) Tiivistelmä

Keksintö koskee maalikoostumusta, joka käsittää sideaineen, kalvonmuodostusaineen sekä mahdollisesti sinänsä tunnettuja lisä- ja apuaineita.

5 Kalvonmuodostusaine koostuu glysidyylietteristä tai -esteristä tai näiden seoksesta, jossa eetterissä tai esterissä alkoholin tai vastaavasti karboksyylihapon hiilivetytähde koostuu 3 - 20 hiiliatomia sisältävästä,

10 lineaarisesta tai haarautuneesta, tyydyttymättömästä tai tyydyttyneestä hiilivedystä. Keksintö koskee edelleen menetelmää maalikoostumuksen kovettumisen nopeuttamiseksi sekä uutta menetelmää glysidyyliesterien valmistamiseksi. Keksinnössä käytettävät

15 kalvonmuodostajat alentavat paremmin kalvonmuodostuslämpötilaa kuin tavanomaiset reaktiiviset kalvonmuodostajat. Alhaisen haihtuvuuden ansiosta yhdisteet soveltuvat käytettäväksi no-VOC -sovel-  
luksissa.

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0-4	Form - PCT/RO/101 PCT Request Prepared using	PCT-EASY Version 2.90 (updated 15.12.1999)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
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I	Title of invention	PAINT COMPOSITIONS
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
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II-7	State of residence	FI
III-1	Applicant and/or inventor	
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## PCT REQUEST

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III-2	<b>Applicant and/or inventor</b>	
III-2-1	This person is:	applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	RISSANEN, Kari
III-2-5	Address:	Hankamäentie 13 FIN-41520 Hankasalmi Finland
III-2-6	State of nationality	FI
III-2-7	State of residence	FI
III-3	<b>Applicant and/or inventor</b>	
III-3-1	This person is:	applicant and inventor
III-3-2	Applicant for	US only
III-3-4	Name (LAST, First)	KOSKIMIES, Salme
III-3-5	Address:	Hämeenapajantie 7 FIN-00850 Helsinki Finland
III-3-6	State of nationality	FI
III-3-7	State of residence	FI
III-4	<b>Applicant and/or inventor</b>	
III-4-1	This person is:	applicant and inventor
III-4-2	Applicant for	US only
III-4-4	Name (LAST, First)	AIROLA, Karri
III-4-5	Address:	Keltavuokontie 4 A 3 FIN-06400 Porvoo Finland
III-4-6	State of nationality	FI
III-4-7	State of residence	FI
III-5	<b>Applicant and/or inventor</b>	
III-5-1	This person is:	applicant and inventor
III-5-2	Applicant for	US only
III-5-4	Name (LAST, First)	JANSSON, Robert
III-5-5	Address:	Honkilahdentie 3 FIN-00940 Helsinki Finland
III-5-6	State of nationality	FI
III-5-7	State of residence	FI

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IV-1	<b>Agent r c mm n representative; r address for correspondence</b> The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	<b>agent</b>
IV-1-1	Name	SEPPO LAINE OY
IV-1-2	Address:	Itämerenkatu 3 B FIN-00180 Helsinki Finland
IV-1-3	Telephone No.	+358-9-68 59 560
IV-1-4	Facsimile No.	+358-9-68 595 610
IV-1-5	e-mail	seppo.laine@selpat.fi
V	<b>Designation of States</b>	
V-1	<b>Regional Patent</b> (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW SD SL SZ TZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT  EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT  EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT  OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT
V-2	<b>National Patent</b> (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AL AM AT AU AZ BA BB BG BR BY CA CH&LI CN CR CU CZ DE DK DM EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW
V-5	<b>Precautionary Designation Statement</b> In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	

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V-6	Exclusion(s) from precautionary designations	NONE	
VI-1	Priority claim of earlier national application		
VI-1-1	Filing date	18 January 1999 (18.01.1999)	
VI-1-2	Number	990089	
VI-1-3	Country	FI	
VI-2	Priority document request The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):	VI-1	
VII-1	International Searching Authority Chosen	Swedish Patent Office (ISA/SE)	
VIII	Check list	number of sheets	electronic file(s) attached
VIII-1	Request	5	-
VIII-2	Description	14	-
VIII-3	Claims	3	-
VIII-4	Abstract	1	nest83.txt
VIII-5	Drawings	1	-
VIII-7	TOTAL	24	
	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-8	Fee calculation sheet	✓	-
VIII-16	PCT-EASY diskette	-	diskette
VIII-17	Other (specified):	Copy of official action	-
VIII-18	Figure of the drawings which should accompany the abstract		
VIII-19	Language of filing of the international application	Finnish	
IX-1	Signature of applicant or agent		
IX-1-1	Name	SEPPO LAINE OY	
IX-1-2	Name of signatory	Jari Lipsanen	

## FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/SE
10-6	Transmittal of search copy delayed until search fee is paid	

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0	<b>For receiving Office use only</b>	
0-1	International Application No.	PCT/FI 0 0 / 0 0 0 3 9
0-2	International Filing Date	18 JAN 2000 ( 1 8. 01. 00 )
0-3	Name of receiving Office and "PCT International Application"	The Finnish Patent Office PCT International Application
0-4	<b>Form - PCT/RO/101 PCT Request</b>	
0-4-1	Prepared using	PCT-EASY Version 2.90 (updated 15.12.1999)
0-5	<b>Petition</b> The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	<b>Receiving Office (specified by the applicant)</b>	National Board of Patents and Registration (Finland) (RO/FI)
0-7	<b>Applicant's or agent's file reference</b>	NEST 83 PCT
I	<b>Title of invention</b>	PAINT COMPOSITIONS
II	<b>Applicant</b>	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	NESTE CHEMICALS OY
II-5	Address:	Keilaniemi FIN-02150 Espoo Finland
II-6	State of nationality	FI
II-7	State of residence	FI
III-1	<b>Applicant and/or inventor</b>	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	SALMI, Maarit
III-1-5	Address:	Tikankolo 9 as 1 FIN-40520 Jyväskylä Finland
III-1-6	State of nationality	FI
III-1-7	State of residence	FI



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IV-1-3	Telephone No.	+358-9-68 59 560
IV-1-4	Facsimile No.	+358-9-68 595 610
IV-1-5	e-mail	seppo.laine@selpat.fi
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IX-1	Signature of applicant or agent		
IX-1-1	Name	SEPPO LAINE OY	
IX-1-2	Name of signatory	Jari Lipsanen	

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(T= 23 °C, rH= 50 %).

